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Determination of  
carbon and sulphur in steel

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DETERMINATION OF CARBON AND SULFUR IN STEEL

BY

ALBERT RUMBLE POLLARD

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THESIS FOR THE DEGREE OF BACHELOR OF ARTS

IN GENERAL SCIENCE

IN THE

COLLEGE OF SCIENCE

OF THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Albert Rumble Pollard.

ENTITLED *Determination of Carbon and*  
*Silicium in Steel*

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF *Bachelor of Arts*

*in General Science*

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## CARBON IN STEEL.

The physical properties, as well as the utility of steel depends to a great extent upon the conditions and amount of carbon present. The total quantity of carbon effects the physical properties in such a way that it may be soft or hard, independent of the other constituents. This fact impresses one with the need of exercising the greatest care in that its determination may be accurate.

There was quite a discussion as to the correct method to be used, up to 1888 when the first committee on international standards was appointed. (1) They chose samples of steel that were to be used in checking up the different methods. They pointed out the errors that were likely to occur when the solution method was used, as the occurrence of pyridine and other tarry products in ammonia cupric chloride. They recommended the use of potassium cupric chloride as it was thought to be pure, but in the work here carbo-hydrates and carbon dioxide were found to be present in the solution. The committee also recommended weighing the potash bulb without a tare, so this work has been done that way.

Today there are many different methods by which carbon may be determined and the following are a few of the methods used:

Eggert's color method (2) is used in the steel laboratories, when a general estimation of the percentage of carbon in a known kind of steel is desired, a standard sample must be run at the same time. It is a great advantage in some work where great speed is required and the estimation does not necessarily need to be close.

Richter's method: (3) In this method the steel is dissolved in an acid solution of potassium cupric chloride, after complete



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solution, which occupies about two hours, the residue is filtered off and determined in any of the following ways:

Combustion in a current of oxygen using a porcelain tube as in Berzelius's method.

Combustion with chromic and sulfuric acids.

Combustion in a current of air and weighing the residue.

Combustion in a Shimer crucible.

Regnault's method: (4) The steel is thoroughly mixed with fifteen times its weight of potassium dichromate, and placed in a clean dry glass tube which is cooled at one end. The tube is heated and the gas absorbed in a potash bulb, after passing through the general drying apparatus. When the flow of gas has ceased, the sealed end is broken and air blown through.

Berzelius's method: (5) In this process the steel is burned directly in a current of oxygen. The sample is finely divided, placed in a boat in a porcelain tube and a current of oxygen passed through. The tube is heated strongly for forty-five minutes, and the carbon dioxide evolved is absorbed in a potash bulb and weighed.

Electric Furnace: (6) The furnace is described by Johnson. It consists of a steel tube containing a non-conducting packing of magnesia, surrounding a smaller quartz tube wound with Hoskin's wire, in which the combustion takes place.

It is stated that the direct combustion method is the most accurate for the determination of carbon in iron and steel, using the solution method for certain alloy steels, as high as 50% of the carbon may be lost. These low results have been explained on the assumption that during solution part of the metallic car-





bides were dissolved passing from the solution as hydrocarbons.

The direct combustion of steel will give higher results than the solution method. Isham and Aumer found that the residue from the direct combustion method contained a very small percentage of carbon. The results obtained from the direct combustion ran about .003% higher than the solution and combustion. The difference was thought to be due to the loss of hydrocarbons during solution, but they were unable to detect any.

The same year Moore and Blair (7) experimented with the loss of carbon during solution. Two samples were used containing respectively 0.65% and 1.18% of carbon. The loss during solution was .05% and .04%.

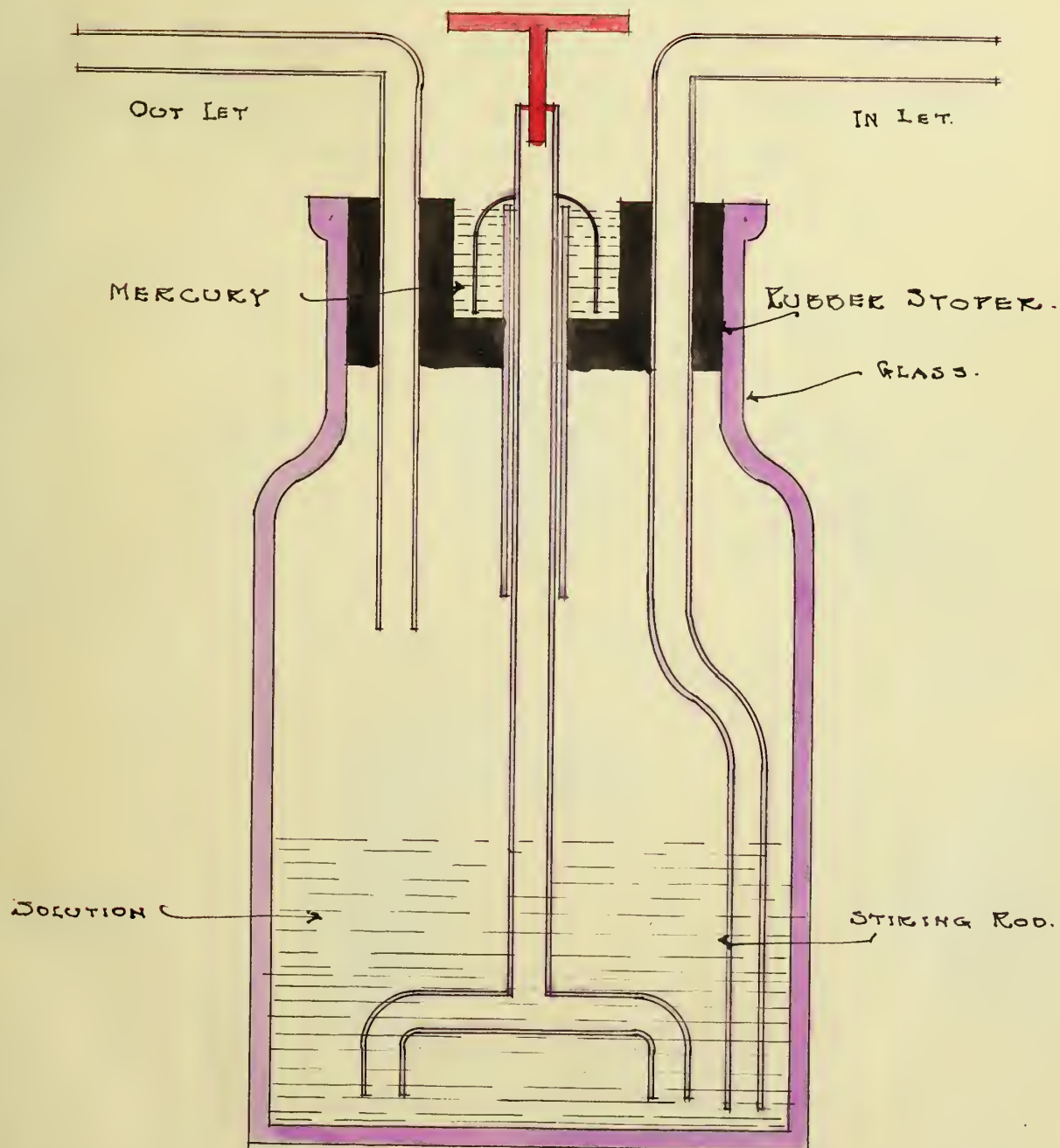
The difference in the results obtained by the above people led to the following experimental work:

The potassium cupric chloride solution was made as follows: 500 grams of the salt were dissolved in 1500 cc of distilled water and 75 cc of concentrated hydrochloric acid. This solution was filtered through asbestos.

The apparatus used consisted of the following:

1. The purifying train, with its two gas wash bottles and a U tube, containing respectively, concentrated sulfuric acid, 30% solution of potassium hydroxide, one bulb of the U tube filled with soda lime and the second calcium chloride, separated by glass wool.
2. A specially constructed apparatus so arranged that air could be blown through the solution and at the same time stirred. (See drawing) A 500 cc wide mouth bottle fitted with inlet and









outlet tubes and a stirrer. The cork is cut into in such a way that the stirring apparatus passes through the center of it, and a seal is made with mercury.

3. A U tube filled with soda lime.

4. The combustion furnace fitted with a Jena hard glass tube, packed with six inches of copper oxide fitted with an asbestos plug before and separating the four inches of lead chromate. This in turn is separated by a plug from a spiral of pure silver foil.

5. A U tube following the furnace fitted with calcium chloride and attached to a potash bulb, containing a 30% solution of potassium hydroxide, fitted with a calcium chloride tube. Following this was another U tube containing in the limb nearest the potash bulb, soda lime, separated from the calcium chloride in the other limb by glass wool.

This apparatus was burned out and tested, and found to be air tight. The furnace was run until the bulb became constant, then 200 cc of the potassium cupric chloride was put into the special apparatus and allowed to run for two hours, with air passing through, when the potash bulb was weighed. Three blanks on the first solution were run, agreeing very closely. A new solution was made and blanks run on it and the increase in weight was very large. Air was then blown through the solution of potassium cupric chloride and the increase in the bulb was found to decrease. Three grams of steel were now put into the apparatus along with 200 cc of the solution. The stirring apparatus caused a constant agitation of the liquid and the solution of the



steel was accomplished in two hours. There was an increase in weight of the bulb greater than the blank, showing a loss of hydrocarbon during solution. The increase in weight could not have been due to carbon dioxide from the air or from the potassium cupric chloride, so must have been due to the combustion of the hydrocarbons, for the soda lime tube preceding the furnace would have absorbed the carbon dioxide. The increase of the blank was not due to chlorine or hydrochloric acid gas, for it would have been absorbed by the substances preceding the potash bulb, as soda lime, copper oxide, lead chromate and pure silver foil. Three samples were used and the following results were obtained:

#### CONCLUSION.

That hydrocarbons are given off during the solution of steel in potassium cupric chloride. That a solution of potassium cupric chloride is not free from volatile hydrocarbons.

#### REFERENCES.

- (1) Jour. of the Amer. Chem. Soc. 1900, page 277
- (2) Jour. of the Amer. Chem. Soc. 1900, page 277
- (3) Chemical News vol. 79, page 167
- (4) Blair's Iron and Steel page 127-69
- (5) Jour. of the Iron and Steel Inst. 1901, page 448
- (6) Jour. of the Amer. Chem. Soc. 1902, page 1206
- (7) Jour. of the Soc. of Chem. Industry vol. 27, page 845





#	Nature of Steel	% Carbon by Soland Comb	% Carbon by Direct Comb.	Gain in KOH blank	Gain in KOH solution	Gain due to CO <sub>2</sub> from Steel	% Loss by Steel	Weight of Steel
1	Bessemer N <sup>o</sup> 2	0.207	0.207	.0045				
2	"	0.189	0.193	.0046				
3	"			.0050				
4	"		Mean	.0047				
5	"				.0100	.0053	.028	5 grams
6	"				.0090	.0043	.023	5 "
7	"				.0080	.0033	.030	3 "
8	"				.0080	.0033	.030	3 "
9	Basic Open hearth N <sup>o</sup> 2	1.048	1.049	New Solution .0032				
10	"							
11	"			.0037				
12	"			.0035				
13	"		Mean	.0034				
14	"				.0070	.0036	.033	3 grams
15	"				.0073	.0039	.035	3 "
16	"	N <sup>o</sup> 6 0.602	0.603					
17	"	0.591	0.589					
18	"				.0060	.0026	.024	3 "
19	"				.0062	.0028	.025	3 "
20	"			.0033				

5A



## SULFUR IN STEEL.

The sulfur content of steel alters its utility to a great extent, more than .1% of sulfur making it hot short. Its determination has been a source of a great amount of experimental work. The large number of determinations required in a short space of time call for faster methods for its determination.

The oxidation and solution (1) or Aqua-regia method is looked upon as the standard.

The evolution method for the determination of sulfur in steel, is based upon the fact, that when drillings are dissolved in hydrochloric acid, hydrogen sulfide is evolved. This gas is absorbed in different solutions according to the operator and determined by some volumetric method.

Professor Lord (2) of Ohio State, passes the evolved gases into an alkaline solution of cadmium chloride and retains the sulfur as cadmium sulfide. The cadmium sulfide is transferred to a beaker, along with the solution, and acidified with hydrochloric acid, then titrated with a standard iodine solution.

Mr. Mathewman (3) obtained the following results when working with the different rates of evolution. He used a pig iron which analyzed to be 0.15% sulfur by the Aqua-regia method.

Rates of Evolution	% Sulfur
Extremely rapid	0.132
Rapid	0.122
Usual rate	0.092
Slow	0.076
Extremely slow	0.049
Extremely slow	0.056





Mr. Williams (4) used Boiling hydrochloric acid in place of the cold acid.

Boiling HCl  
% S

0.064  
0.049  
0.057  
0.013  
0.060  
0.186  
0.097

Cold HCl and Slow Evolution  
% S

0.051  
0.039  
0.049  
0.008  
0.050  
0.159  
0.087

The above work was on seven different samples.

Boiling con. HCl and  
boiling water  
% S

0.049  
0.050  
0.051

Cold HCl and Slow Evolution  
% S

0.030  
0.034

Boiling dilute HCl

% S

0.044

The last was on one sample.

In order to expel the gas from the train, carbon dioxide is used. Blair used hydrogen while Dudley (5) states that neither gas has any advantage over air.

Phillips (6) tries to show that sulfur is combined in some organic compounds as  $\text{CH}_3\text{HS}$ . He passes the evolved gases through a heated tube in the presence of carbon dioxide. The solution of steel by means of hydrochloric acid was boiled until all of the oily drops disappeared. The gas was passed into a solution of bromine water acidified with hydrochloric acid and then into an eight litre bottle containing bromine solution, oxidizing it to sulfuric acid. The following results were obtained:



Standard Evo- lution method	Passing the gas through a heated tube.	Aqua-regia (Plair)
g S	g S	g S
0.059	0.096	0.101
0.046	0.095	0.098
0.050	0.098	0.098
0.054	0.098	0.098
<u>0.055</u>	0.104	0.100
	0.104	0.100
	0.099	0.102
	0.100	0.102
	<u>0.107</u>	0.104
Mean 0.052	0.099	0.100

SAMPLE B.

0.100	0.183	0.175
0.101	0.178	0.170
0.087	0.175	0.168
0.092	0.177	0.170
0.092	0.180	0.174
0.084	<u>0.181</u>	0.171
Mean 0.094	0.180	0.171

Jaboulay (7) modified the evolution method in such a way that the evolved gases on passing through the apparatus came in contact with a jet of burning hydrogen in the presence of air. Here sulfur dioxide was formed, this was passed into hydrogen peroxide forming sulfuric acid, and precipitated as barium sulfate. He claims to catch some of the organic compounds of sulfur in this way. He did not tabulate any of his results.

In the usual mode of conducting the method, the impure hydrogen sulfide that is evolved, is led into an absorbing apparatus and the sulfur content determined by oxidation and precipitation as barium sulfate or by some volumetric method. In the laboratories of the iron and steel industries, it is a generally recognized fact that in the use of the evolution method for certain cast irons, notably those that contain a high percentage of



carbon, some sulfur is lost, and in cases where great accuracy is required the Aqua-regia method is much better. It is common to find that during the solution of steel in hydrochloric acid, there is produced a considerable quantity of ill-smelling hydro-carbons. The inner surface of the flask becomes coated with minute globules of an oily substance that is not miscible in water.

There can be little doubt that the loss of sulfur which results in the determination is dependent upon the formation of this organic compound during the solution. It has been attempted to explain the loss of sulfur on the hypothesis that sulfur exists in iron and steel in more than one compound, and that all of it is not converted into hydrogen sulfide, but that part of it remains in the flask and solution. The fact that a portion only of the sulfur in white cast iron is liberated as hydrogen sulfide, by acids, suggests that the molecules do not contain all of its sulfur linked in the same manner.

The sulfur content of three government steel samples was determined by several different methods, so that their efficiency could be determined.

1. The sulfur content was determined by the Aqua-regia method.

2. The standard evolution method used was as follows:  
A 300 cc flask was used, to which was attached a hydrogen generator, a return condenser and a glass stoppered funnel. The condenser was then connected, by means of glass tubing, to a nitrogen flask containing 25 cc of a solution of cadmium chloride. This in turn was connected to another nitrogen flask containing the same amount of solution. The train was tested for leaks





and found to be air tight, a stream of hydrogen was passed through the apparatus for ten minutes. The two nitrogen flasks were then attached, the hydrogen turned off, and dilute hydrochloric acid added by means of the glass stoppered funnel, to the steel in the flask. When the solution was complete, it was boiled until all of the oily globules disappeared. The train was freed from hydrogen sulfide by means of a stream of hydrogen. The contents of both nitrogen flasks were washed into a large porcelain dish, first by water, then dilute hydrochloric acid and finally with water. The solution was then acidified with hydrochloric acid and titrated with a standard iodine solution, using starch as an indicator.

The iodine solution used was as follows:

Iodine	5.956 gr.
Potassium iodide (Iodate free)	2.200 gr.
Water (distilled)	10.00 cc.

This was set aside until the solution was complete, then made up to a litre, being standardized by means of sodium thiosulfate and potassium dichromate.

It is generally understood that a new solution of iodine will change, so to verify the results, the solution was standardized on the following days.

Dates	Factor weight
Nov. 23, 1909	5.0761 grams
24, "	5.0761 "
30, "	5.0761 "
Dec. 1, "	5.0761 "
14, "	5.0556 "
Jan. 4, 1910	5.1020 "
10, "	5.1020 "
20, "	5.1020 "
Feb. 26, "	5.0525 "
April 4, "	5.0040 "



Cadmium Chloride Solution.

Cadmium chloride	80.0 g.
Ammonium hydroxide	1000.0 cc.
Water	1000.0 cc.

3. The previous method was used, but boiling acid was substituted for the cold acid. The percentage of sulfur running a little higher.

4. The same apparatus as in the evolution method was used but a furnace containing a Jena glass tube was inserted between the condenser and nitrogen flask. The hydrogen sulfide and excess of hydrogen along with the volatile organic sulfur compounds were passed through the glass tube heated to a dull red. The organic compounds are decomposed into hydrogen sulfide.

5. Carbon dioxide was substituted for hydrogen, but as it was passed into an alkaline solution, carbonates were formed and when the hydrochloric acid was added, to the contents of the nitrogen flask, carbon dioxide was evolved. The sulfur was then determined as in the previous method and the percentage was found to run low. This was probably due to some of the hydrogen sulfide being carried off with the carbon dioxide mechanically. This could have been carried out in acid solution.

6. An effort was made to determine the sulfur content of steel by direct combustion. Burning it in a "Gooch" platinum crucible, such as is used for moisture determination in mineral analysis, in the presence of oxygen. The sulfur is burned to sulfur dioxide, then passed into a hydrogen peroxide solution, when it is oxidized to sulfuric acid. In order to do this work a highly acid clay was obtained, for it was thought that the sul-





fur would not be retained by it, as was the case when a basic clay was used.

An amount of clay was digested with water and hydrochloric acid, to wash out the sulfur but this was found to be impossible. A new portion was mixed with water, making a thick paste, and moulded into pellets. Two of the clay pellets were heated in a "Rose" crucible in the presence of oxygen for thirty and sixty minutes respectively. The combustion of carbon was found to be completed after sixty minutes. The steel did not run into the pellet and could be easily separated.

A platinum pail was made to fit into the "Gooch" crucible and into this the clay pellet, containing a known weight of steel was put. The cover of the crucible was sealed on with sodium metatungstate, all the connections were made tight and tested. Oxygen was passed through the purifying train, composed of gas wash bottles containing sulfuric acid, potassium hydroxide and a U tube containing soda lime and calcium chloride. Blanks were run on both the oxygen and hydrogen peroxide. The inlet and outlet tubes were joined to the platinum crucible by means of lead glass. Attached to the outlet tube was a nitrogen flask containing hydrogen peroxide acidified with hydrochloric acid. The sulfur dioxide formed by burning the sulfur was oxidized to sulfuric acid by passing the gas into hydrogen peroxide, and precipitated by means of barium chloride. The heating of the crucible was for different durations of time, and in some cases the residue was analyzed for the sulfur content by the Aqua-regia method. The steel was found to contain some sulfur. The sulfur content of the clay had increased. After subtracting the weight of bar-



ium sulfate in the hydrogen peroxide blank, some was left showing that it was possible to burn out a small percentage of sulfur.

A pellet was burned for eighteen hours, but still contained some sulfur which was evolved at a regular rate, as was determined by passing the gas into hydrogen peroxide. The steel was then put into the pellet and burned for three hours. The amount of sulfur evolved was very small. The steel retained some of its sulfur content, while the sulfur content of the pellet increased.

#### CONCLUSION.

The determination of sulfur in steel by passing the evolved gases through a heated tube gives the most accurate results, for even in the Aqua-regia method, some of the sulfur may be lost.

The direct combustion for the determination of sulfur is incomplete, for it is impossible to burn out all of the sulfur.

#### REFERENCES.

- |  |                  |
|--|------------------|
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| (2) Lord's Metallurgical Analysis        | page 107         |
| (3) Jour. of the Am. Foundrymens Assoc.  | 1903 page 243    |
| (4) Eng. of Western Pa.                  | vol. 8 page 863  |
| (5) Pamphlet issued by Pa. R. R.         |                  |
| (6) Jour. of the Amer. Chem. Soc.        | 1895 page 891    |
| (7) Reve generale de chimie pure et appl | vol. 10 page 193 |



# BESSEMER STEEL

Aqua-Regia %S	Evolution %S	Evolution With Boiling HCl %S	Evolution with Hot Tube using Hydrogen %S	Evolution with Hot Tube using CO <sub>2</sub> %S
0.081	0.080	0.080	0.085	0.069
0.082	0.079	0.079	0.084	0.071
		0.079	0.086	0.075
			0.096	
			0.094	
			0.083	
			0.081	
			0.083	
			0.083	
Mean 0.082	0.080	0.079	0.083 <sup>2</sup>	0.072

## Sample B

0.116	0.105	0.107	0.116	
0.117	0.104	0.108	0.118	
		0.109		
Mean 0.117	0.105	0.108	0.117	

## Basic Open Hearth Steel

0.024	0.019	0.030	0.036	
0.028	0.014	0.032	0.036	
	0.020	0.033	0.041	
	0.011	0.034	0.036	
	0.011	0.034	0.033	
	0.020			
	0.016			
Mean 0.026	0.016	0.032	0.036	



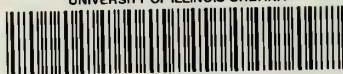








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